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(54) NOZZLE PLATE, LIQUID EJECTING HEAD, AND LIQUID EJECTING APPARATUS

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(51) **Int. Cl.**

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B41J 2/045	(2006.01)
B41J 2/16	(2006.01)

(52) **U.S. Cl.**

CPC ***B41J 2/14233*** (2013.01); ***B41J 2/1433*** (2013.01); ***B41J 2/161*** (2013.01); ***B41J 2/162*** (2013.01); ***B41J 2/1623*** (2013.01); ***B41J 2/1626*** (2013.01); ***B41J 2/1642*** (2013.01); *B41J 2002/14241* (2013.01); *B41J 2002/14419* (2013.01); *B41J 2002/14491* (2013.01); *B41J 2202/03* (2013.01)

USPC **347/47**; 347/68

(58) **Field of Classification Search**

None

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

8,567,909	B2 *	10/2013	Sieber	347/45
2005/0001879	A1	1/2005	Miyajima et al.	

FOREIGN PATENT DOCUMENTS

JP	2003-072086	3/2003
JP	2004-351923	12/2004
JP	2009-119724	6/2009
JP	2009-184176	8/2009

* cited by examiner

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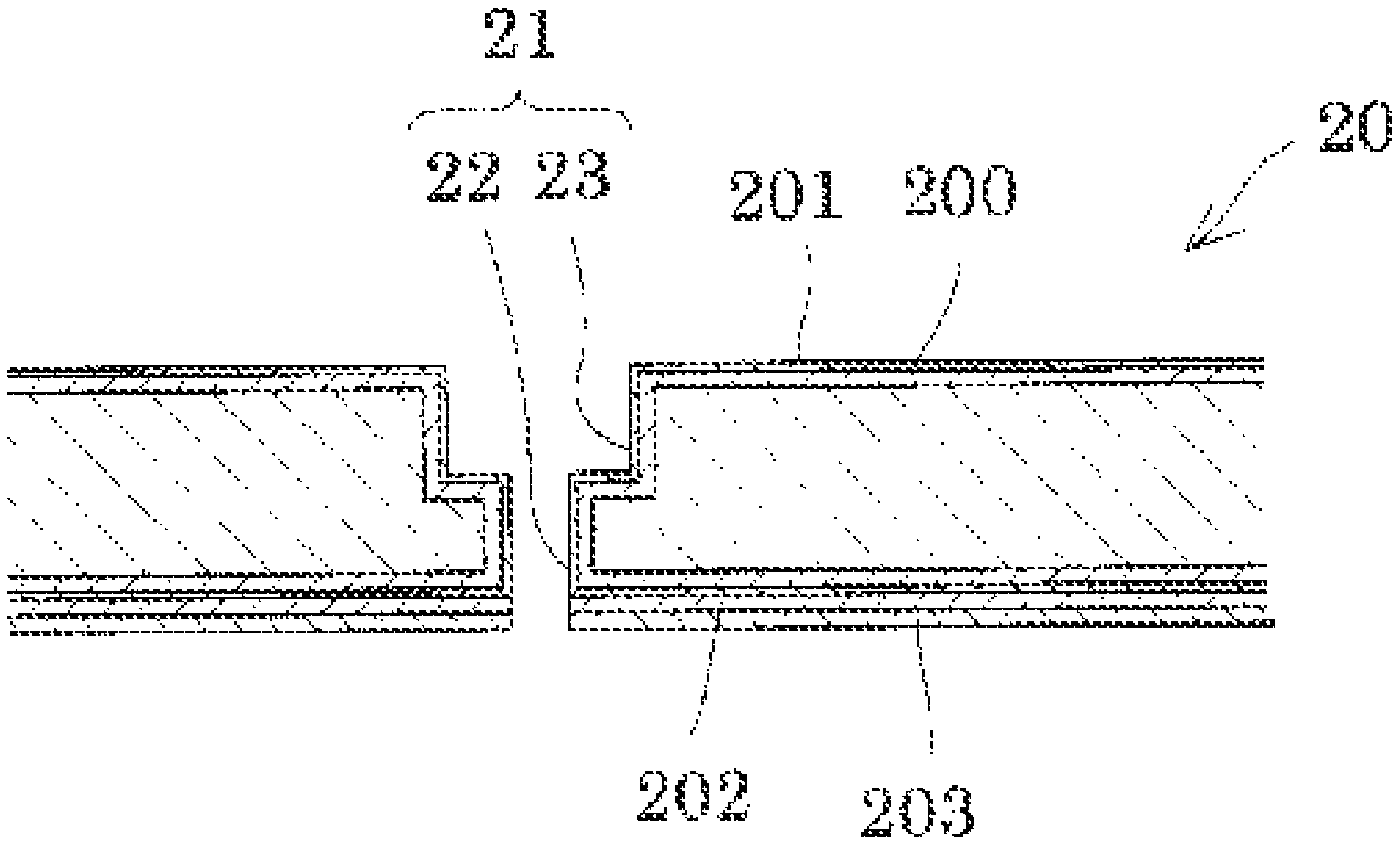
(57) **ABSTRACT**

A silicon nozzle plate has excellent liquid resistance on an inner surface of a nozzle opening and a discharge surface. A plurality of the nozzle openings are disposed in a silicon substrate of the nozzle plate. A first tantalum oxide film is disposed by atomic layer deposition on both surfaces of the silicon substrate and the inner surface of the nozzle opening, and a second tantalum oxide film that is formed by plasma CVD is stacked on the first tantalum oxide film of the discharge surface.

15 Claims, 6 Drawing Sheets



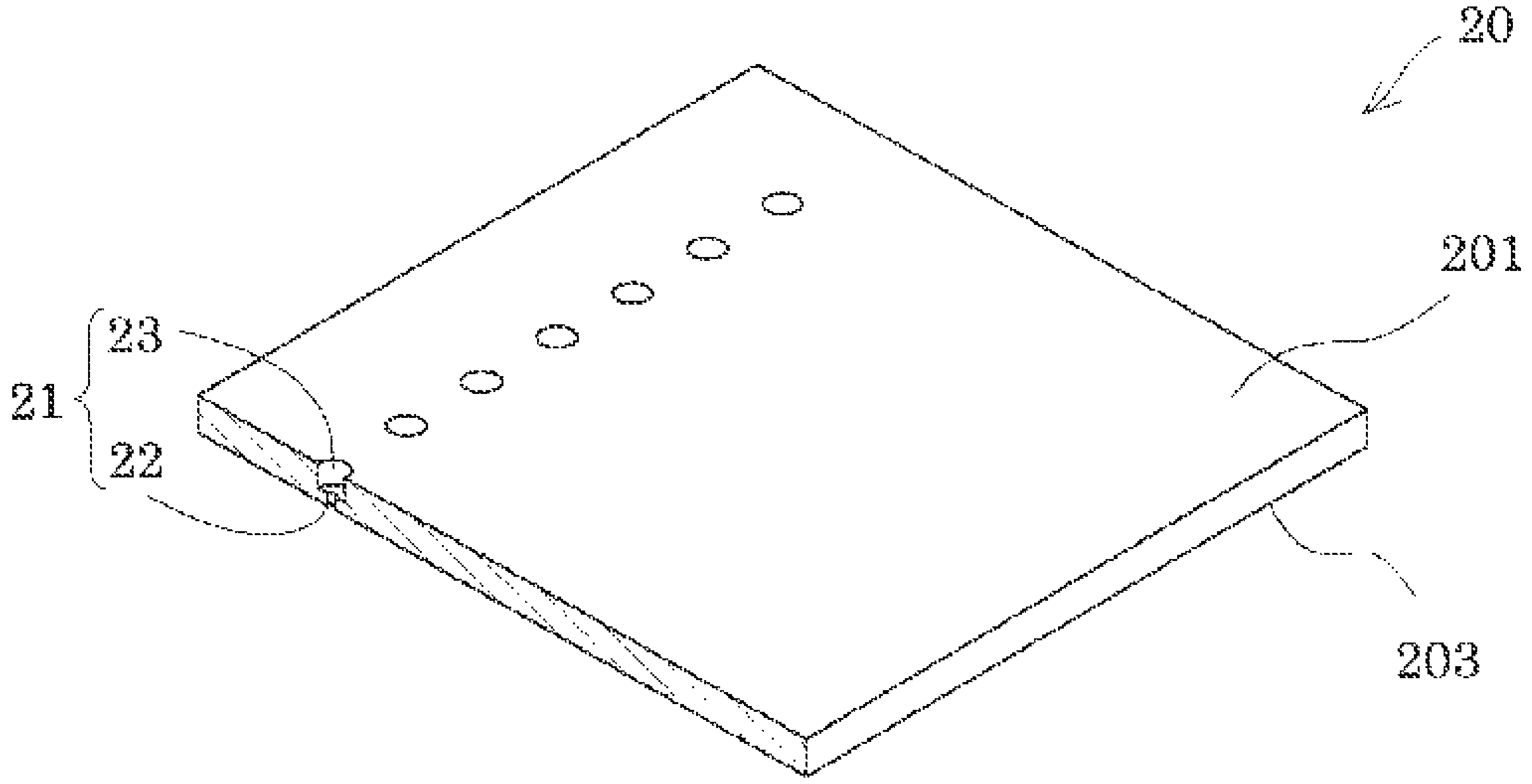


FIG. 1A

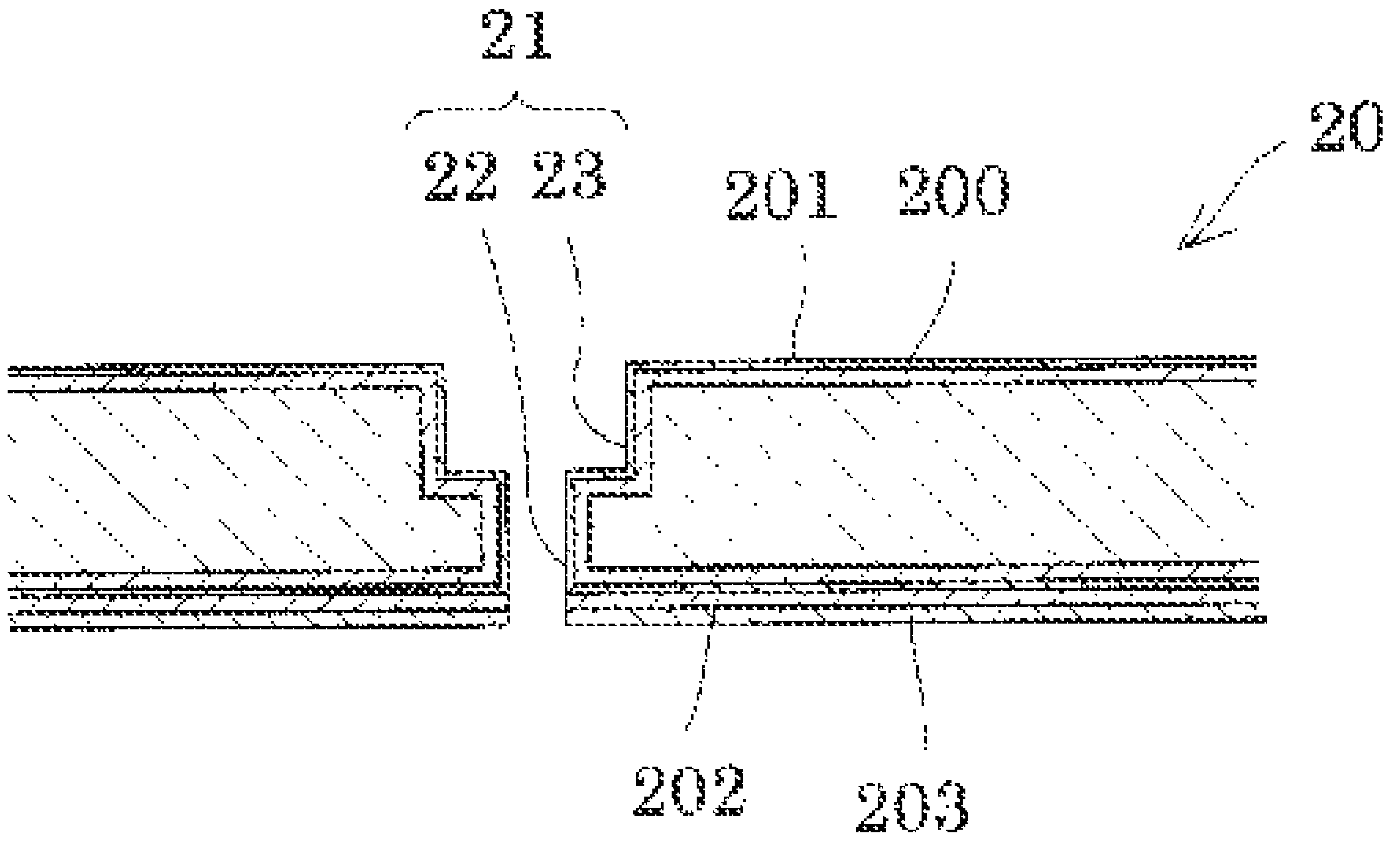


FIG. 1B

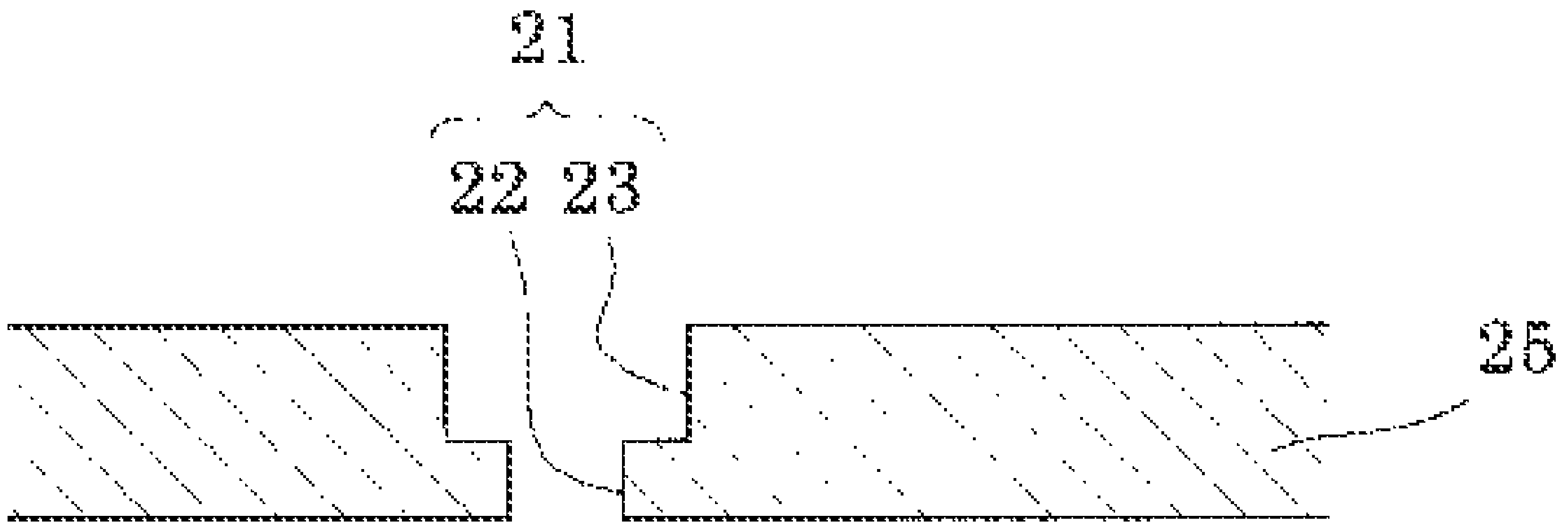


FIG. 2A

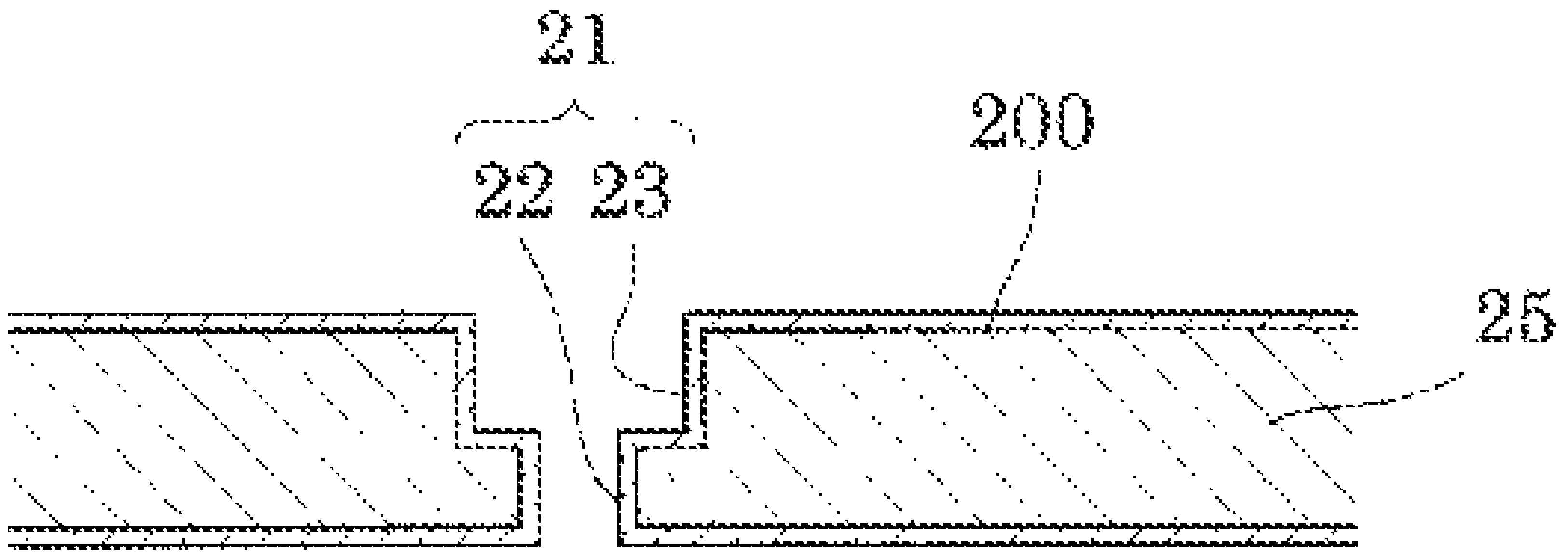


FIG. 2B

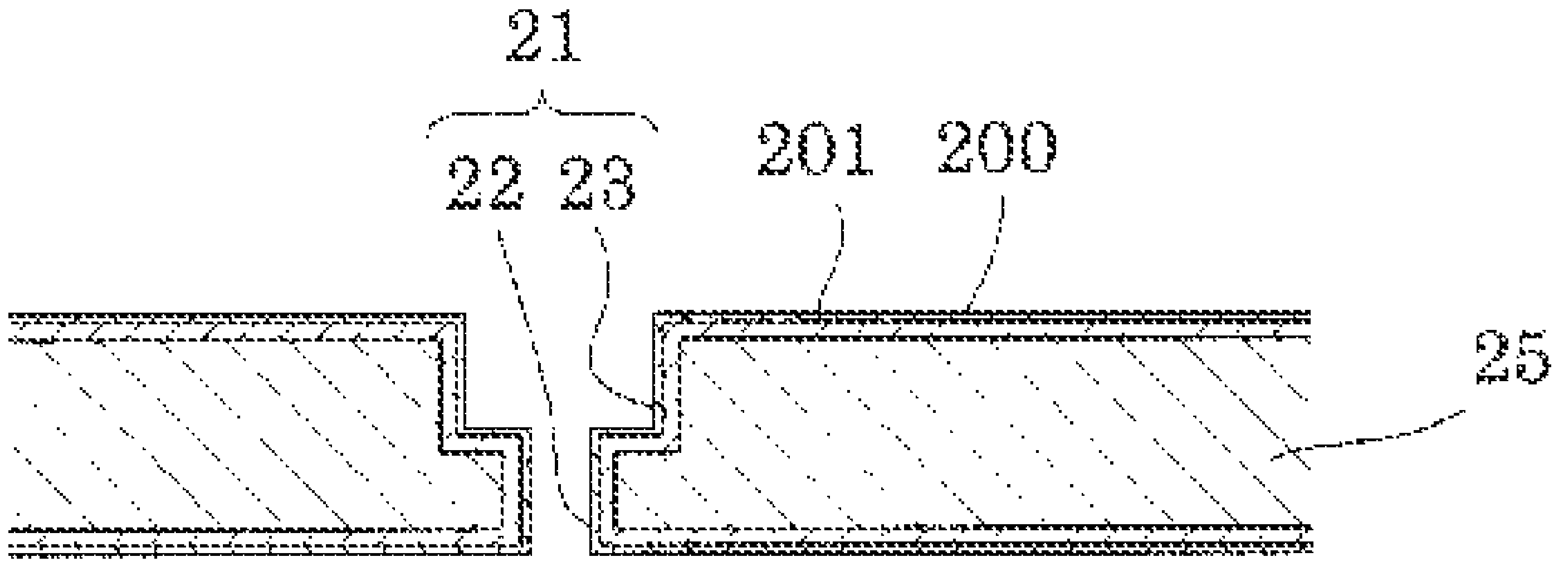


FIG. 2C

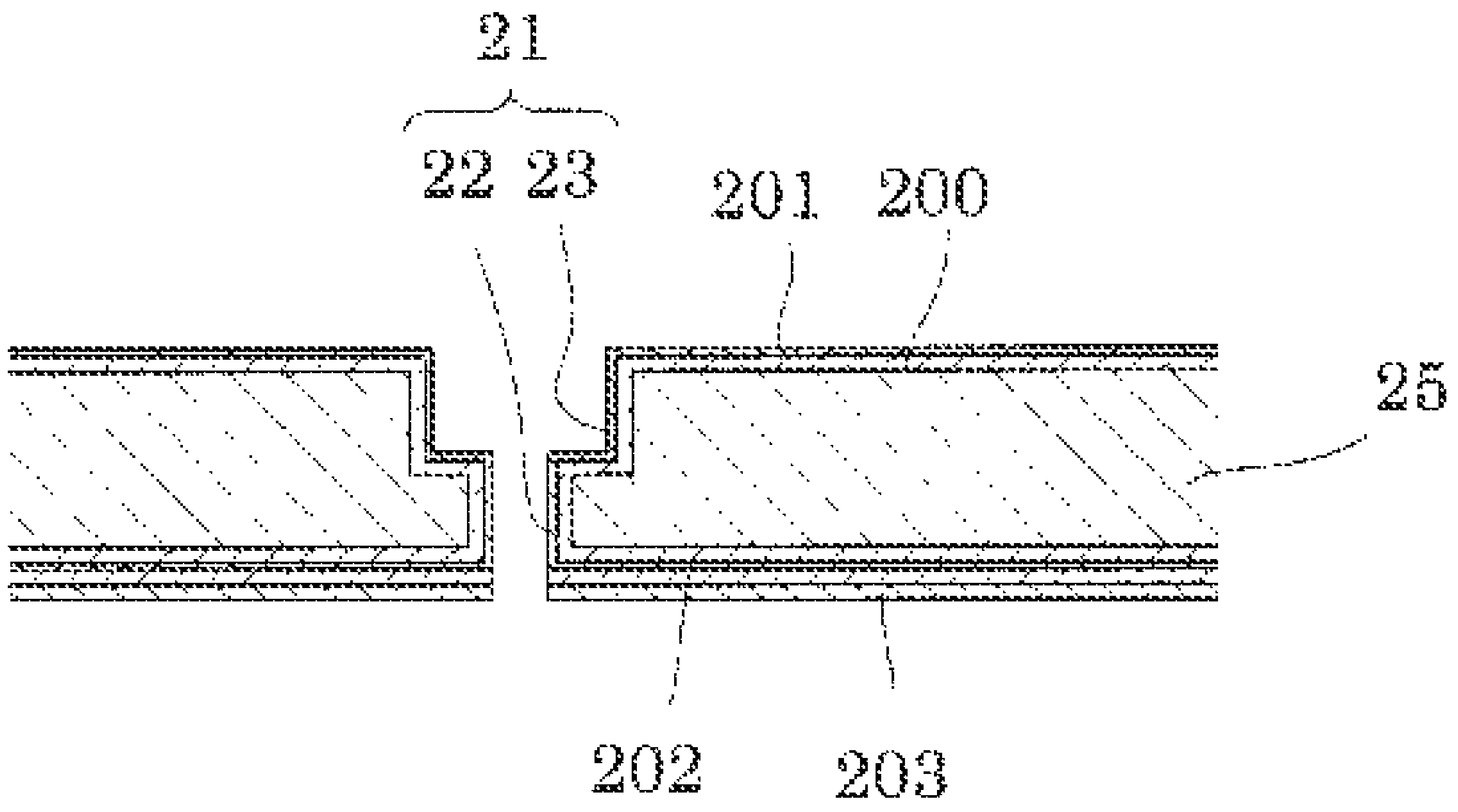
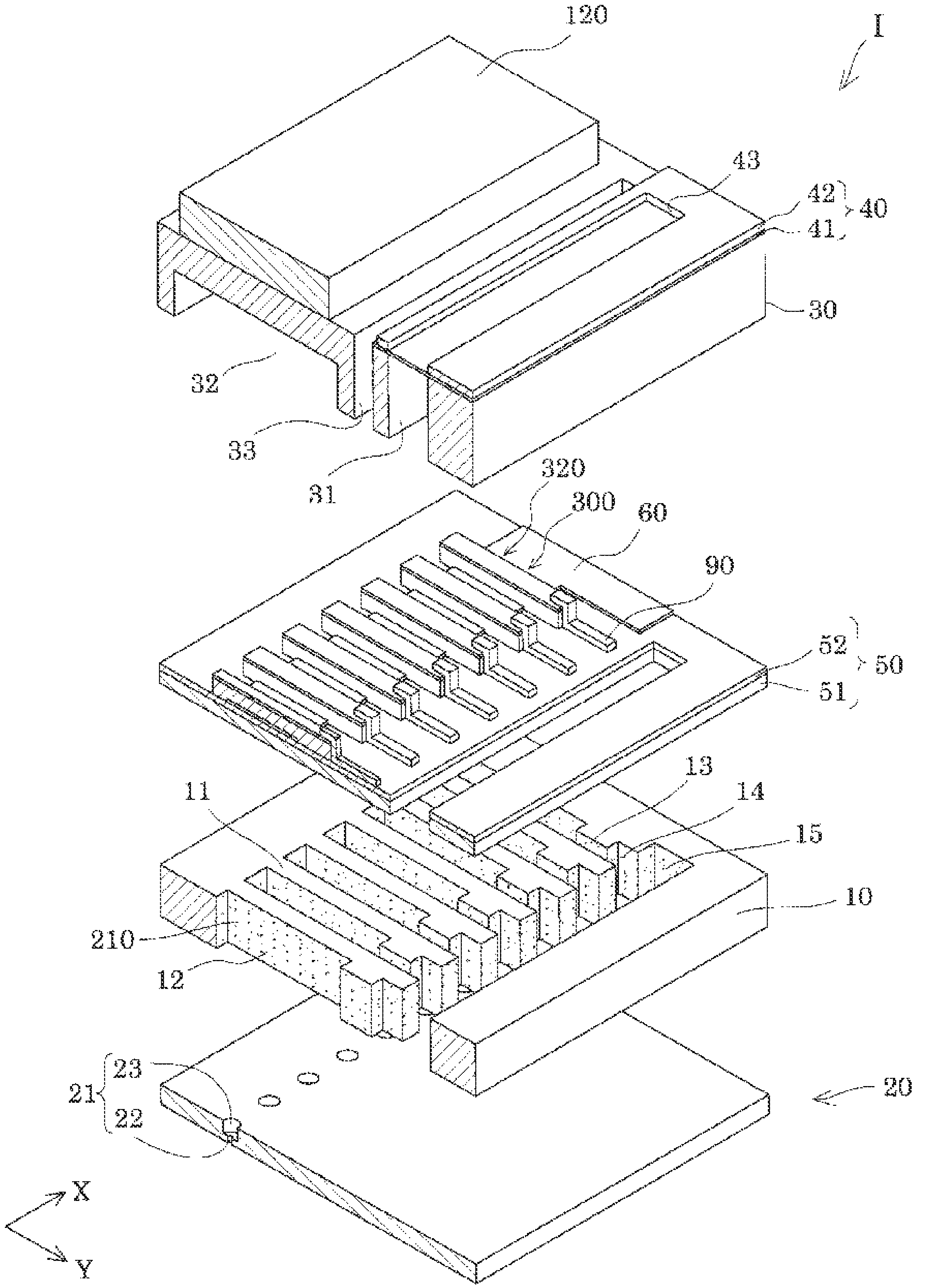


FIG. 2D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I
43
42
40
41
30
32
33
31
320
300
60
90
52
50
51
11
13
14
15
10
210
12
23
21
22
20
X
Y

FIG. 3

FIG. 4A

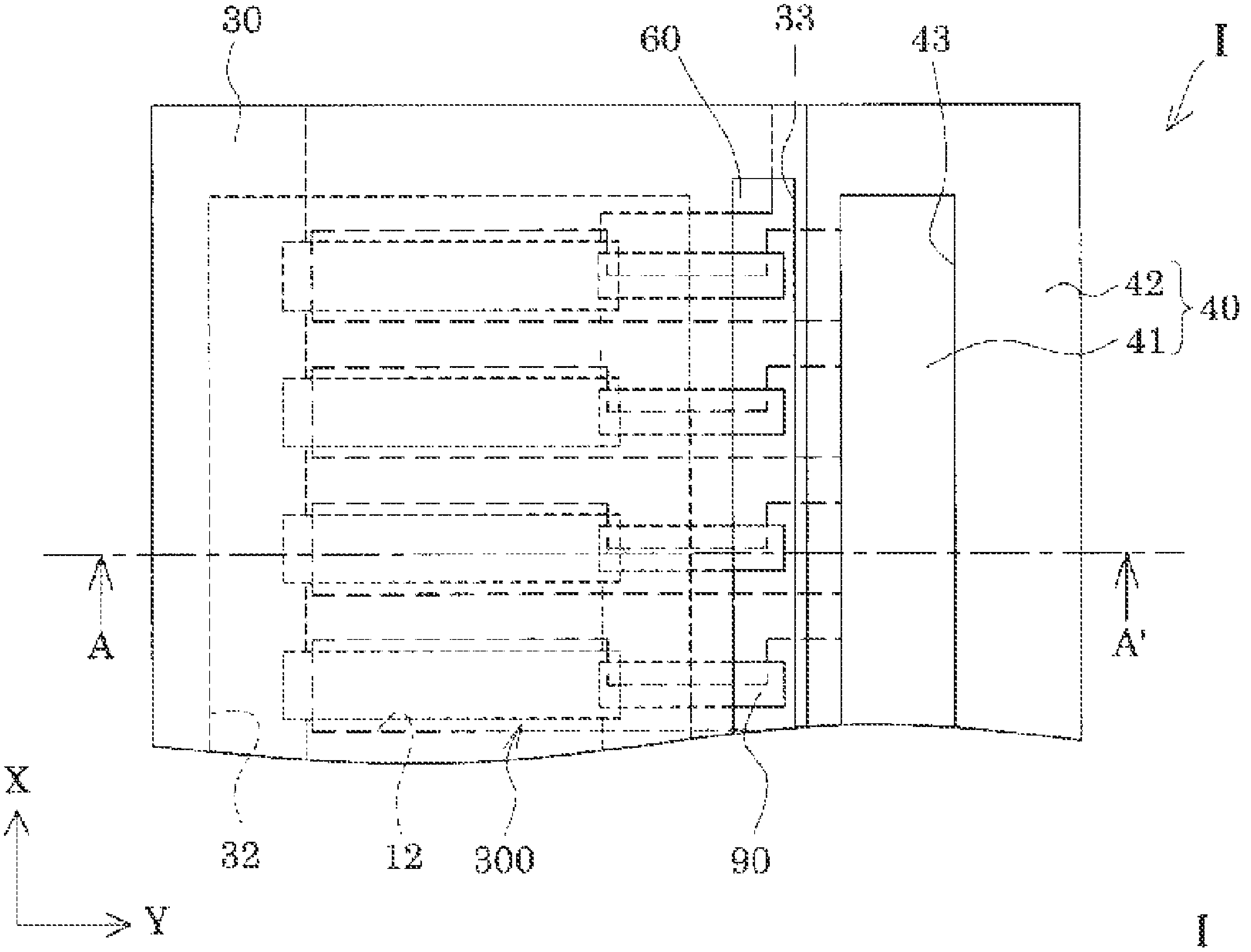
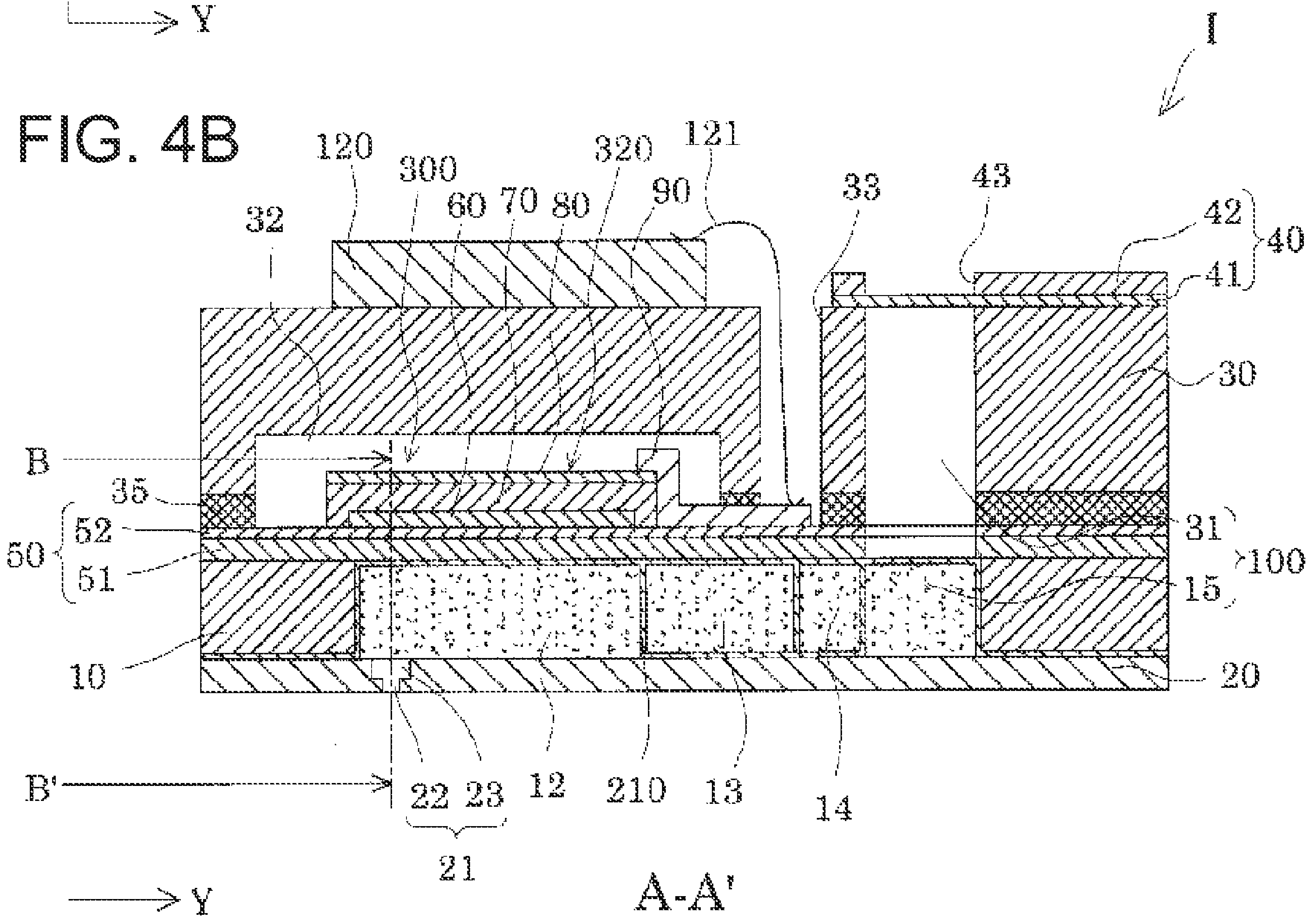

30
60
33
43
I
42
41
40
A
A'
X
Y
32
12
300
90

FIG. 4B


I
120
300
320
121
32
60
70
80
90
33
43
42
41
40
30
B
35
52
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B'
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23
21
12
210
13
14
Y
A-A'

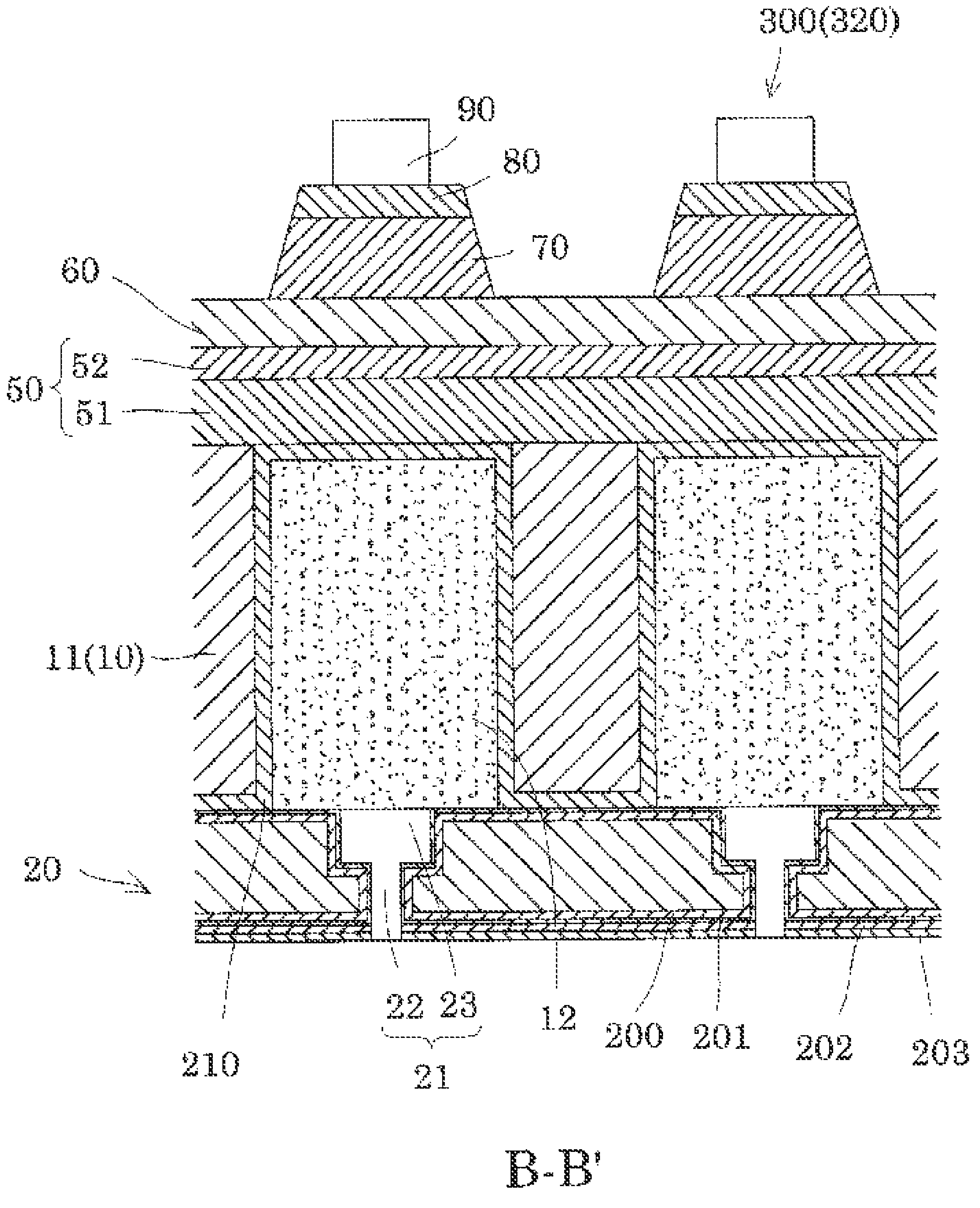
300(320)
90
80
70
60
50
52
51
11(10)
20
210
22
23
21
12
200
201
202
203
B-B'
X

FIG. 5

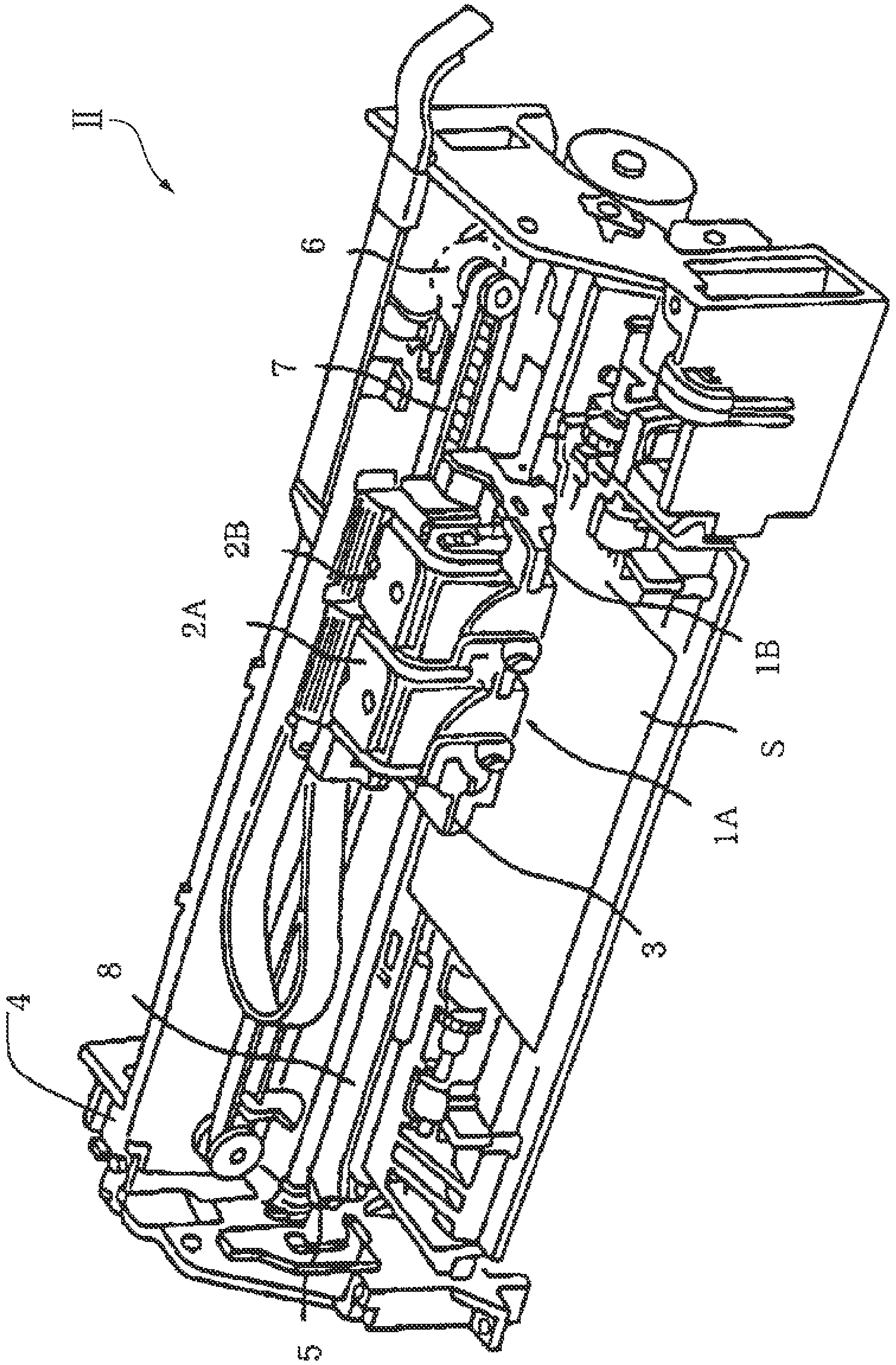

FIG. 6

NOZZLE PLATE, LIQUID EJECTING HEAD, AND LIQUID EJECTING APPARATUS

BACKGROUND

1. Technical Field

The present invention relates to a nozzle plate having a nozzle opening to discharge liquid drops, and a liquid ejecting head and a liquid ejecting apparatus including the nozzle plate.

2. Related Art

In general, an ink jet type recording head known as a representative example of a liquid ejecting head includes a nozzle plate where a plurality of nozzle openings to discharge liquid drops are formed, and a passage forming substrate where a pressure generating chamber communicating with the nozzle opening is formed. In such a liquid ejecting head, a silicon substrate is used in the passage forming substrate and the nozzle plate for an increase in nozzle density, and both thereof are bonded with each other by an adhesive agent.

JP-A-2009-184176 discloses a method for suppressing residue of the ink, in which a surface of a nozzle plate bonded with the passage forming substrate and an inner surface of the nozzle opening are provided with a first ink-resistant protective film formed from an oxide silicon film by thermal oxidation, and a second ink-resistant protective film formed from metal oxide such as a tantalum pentoxide film formed by thermal CVD and plasma CVD and, further, a third ink-resistant protective film (base film) formed from metal oxide such as a tantalum pentoxide film formed by thermal CVD and plasma CVD and a water-repellent film (ink-repellent film) are formed on an ink discharge surface.

Also, JP-A-2004-351923 discloses a structure in which a base film such as a plasma-polymerized film of a silicone material and a liquid-repellent film disposed on the base film such as a metal alkoxide-polymerized molecular film are disposed as the liquid-repellent film of a nozzle discharge surface.

However, there is a case where a uniform film is unlikely to be formed on the inner surface of the nozzle opening, particularly around the vicinity of the discharge surface, and an ink resistance problem is likely to occur when the ink-resistant protective film formed of the metal oxide is disposed by CVD, and where film thickness is likely to be large and not uniform and a problem of non-uniformity of discharged ink drops arises when a sufficient film is to be formed over the entire surfaces. In a case where the above-described nozzle plate is a nozzle plate in which a nozzle hole is formed on the silicon substrate by using anisotropic etching, there is a case where an adhesive property of the ink protective film causes a problem.

In addition, the base film such as the plasma-polymerized film of the silicone material of JP-A-2004-351923 has a possibility of generating microdefects, and there is a case where a problem such as peeling of the liquid-repellent film arises due to such microdefects.

SUMMARY

An object of the invention is to provide a nozzle plate that has excellent liquid resistance on an inner surface of a nozzle opening and a discharge surface, and a liquid ejecting head and a liquid ejecting apparatus using the nozzle plate.

An aspect of the invention is directed to a nozzle plate in which a plurality of nozzle openings are disposed in a silicon substrate, in which a tantalum oxide film formed by atomic layer deposition is disposed on both surfaces of the silicon substrate and an inner surface of the nozzle opening, and a tantalum oxide film formed by plasma CVD is stacked on the tantalum oxide film of a discharge surface.

According to this aspect, the tantalum oxide film that is film-formed by an atomic layer deposition method is uniformly and densely formed even on a narrow area such as an inner circumferential surface of the nozzle opening, and functions effectively as the protective film against a strong alkaline liquid and a strong acid solution since the tantalum oxide film formed by plasma CVD is stacked thereon. Also, since the tantalum oxide film formed by plasma CVD which is a base of the liquid-repellent film is disposed on the tantalum oxide film which is film-formed by the atomic layer deposition method, the adhesive property is excellent when the thick liquid-repellent film excellent in mechanical strength and liquid resistance is disposed.

It is preferable that a thickness of the tantalum oxide film formed by the atomic layer deposition is within a range of 0.3 Å to 50 nm, and a thickness of the tantalum oxide film formed by the plasma CVD is within a range of 200 nm to 1,000 nm. In this case, liquid resistance is sufficiently ensured, and an open state in the nozzle opening is not affected.

It is preferable that a silicon thermal oxide film is formed in a lower layer of the tantalum oxide film formed by the atomic layer deposition. In this manner, liquid resistance can be further improved.

It is preferable that a liquid-repellent film is stacked on the tantalum oxide film formed by the plasma CVD through annealing of a metal alkoxide film. In this case, liquid repellency of the discharge surface is improved, high liquid resistance is ensured in a part where the liquid-repellent film is not formed in a boundary portion between an inner portion of the nozzle opening and an area in the vicinity of the nozzle opening where the liquid-repellent film is formed, and a problem such as peeling of the liquid-repellent film caused by a problem such as erosion of the silicon substrate by a liquid is addressed.

Another aspect of the invention is directed to a liquid ejecting head including the nozzle plate of the above aspect, a passage forming substrate where a pressure generating chamber that is bonded with the nozzle plate and communicates with the nozzle opening is disposed, and a pressure generation unit that is disposed on an opposite side to the nozzle plate of the passage forming substrate to generate a pressure change in the pressure generating chamber.

According to this configuration, the nozzle plate is excellent in liquid resistance and has no problem of peeling of the liquid-repellent film, and opening variation of the nozzle opening is small, and thus a liquid ejecting head with little discharge variation and excellent in durability can be achieved.

Still another aspect of the invention is directed to a liquid ejecting apparatus including the liquid ejecting head of the above aspect. According to this, a liquid ejecting apparatus with little discharge variation and excellent in durability can be achieved.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described with reference to the accompanying drawings, wherein like numbers reference like elements.

FIGS. **1**A and **1**B are a perspective view and an enlarged cross-sectional view of a main part of a nozzle plate according to Embodiment 1.

FIGS. **2**A to **2**D are views showing processes of manufacturing the nozzle plate according to Embodiment 1.

FIG. **3** is an exploded perspective view of a recording head according to Embodiment 2.

FIGS. **4**A and **4**B are a plan view and a cross-sectional view of the recording head according to Embodiment 2.

FIG. **5** is a cross-sectional view of the recording head according to Embodiment 2.

FIG. **6** is a schematic structural view of a recording apparatus according to an embodiment.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

Embodiment 1

First, an example of a nozzle plate according to Embodiment 1 of the invention will be described. FIGS. **1**A and **1**B are a perspective view and an enlarged cross-sectional view of a main part of the nozzle plate according to Embodiment 1.

As shown in FIGS. **1**A and **1**B, the nozzle plate **20** is a member formed from a silicon single crystal substrate on which a plurality of nozzle openings **21** are formed in a row with a pitch corresponding to a dot formation density. In this embodiment, a nozzle array is configured such that the number of the nozzle openings **21** arrayed with a pitch of 180 dpi is 180. Each of the nozzle openings **21** is configured to have two successive cylindrical hole portions that are formed by dry etching and have different inner diameters. In other words, the nozzle opening **21** is configured to have a first cylindrical portion **22** that is formed on an ink discharge side in a plate thickness direction of the nozzle plate **20** and has a small inner diameter, and a second cylindrical portion **23** that is formed on an opposite side (ink passage side) from the ink discharge side and has a large inner diameter. The formation of the nozzle opening **21** is not limited to what is shown in the drawings. For example, the nozzle opening **21** may be configured to have a cylindrical portion (straight portion) with a constant inner diameter, and a tapered portion whose inner diameter is gradually increased from an ejection side toward the ink passage side. A silicon thermal oxide film **200** and a protective film **201** that is formed from a tantalum oxide film which is formed by atomic layer deposition are sequentially formed on both surfaces of the nozzle plate **20** and an inner circumferential surface of the nozzle openings **21**. In addition, a tantalum oxide-containing base film **202** that is formed by plasma CVD and a liquid-repellent film (silane coupling agent (SCA) film) **203** that is formed through a drying treatment, an annealing treatment, and the like after film formation of a molecular film of metal alkoxide having liquid repellency are sequentially stacked on an ink discharge side surface (hereinafter referred to as "discharge side surface") of the nozzle plate **20**. Being formed by plasma CVD refers to being film-formed by a plasma CVD method.

Herein, the silicon thermal oxide film **200** is formed by thermally oxidizing a silicon substrate, and is formed on both of the surfaces of the nozzle plate **20** and the inner circumferential surface of the nozzle opening **21**. The thickness thereof is, for example, approximately 100 nm.

The thermal oxide film **200** does not necessarily need to be disposed. In this case, the protective film **201** is formed directly on the silicon substrate. Even in a case where the thermal oxide film **200** is not disposed, there is a case where a silicon natural oxide film is formed between the silicon substrate and the protective film **201**, which is also included in the invention.

The protective film **201** contains tantalum oxide (TaOx) that is represented by tantalum pentoxide. The protective film **201** is formed by atomic layer deposition, can be formed to have a thin film thickness compared to a film which is formed by another gas phase method such as a CVD method, and can be formed with reliability and a uniform film thickness also on the inner circumferential surface of the small nozzle opening **21**. Being formed by atomic layer deposition refers to being film-formed by an atomic layer deposition method (ALD method). Further, the ALD method has an advantage that the formation can have high film density. In other words, by forming the protective film **201** with high film density, the ink resistance (liquid resistance) of the protective film **201** can be improved such that erosion of the silicon substrate by ink (liquid) can be suppressed. In particular, the protective film **201** is formed with reliability and high film density even on the inner circumferential surface of the nozzle opening **21** vulnerable to an ink resistance problem and a corner portion of a boundary between a discharge surface side face and the nozzle opening **21**, and thus the ink resistance of the nozzle plate **20** is significantly improved.

The thickness of the protective film **201** may be within a range of 0.3 Å to 50 nm, preferably within a range of 10 nm to 30 nm. The protective film **201** that is formed by the atomic layer deposition method in this manner is a film substantially thinner than an approximately 100 nm-thick film formed by a CVD method or the like. If the film is thinner than this, there is a possibility that the film is formed not to be completely uniform. If the film is thicker than this, the film formation becomes time-consuming and costly, which is not preferable, either.

The base film **202** is a tantalum oxide film that is film-formed by plasma CVD, and has an excellent adhesive property to not only the protective film **201** but also the liquid-repellent film **203**. The thickness of the base film **202** is within a range of 200 nm to 1,000 nm, which contributes to improvement in the mechanical strength of a discharge surface. Compared to the ALD method, the film formation by plasma CVD has a significantly higher film formation rate, and even the base film **202** with a thickness of between 200 nm and 1,000 nm can be film-formed within a relatively short period of time.

The liquid-repellent film **203** is a molecular film that is film-formed through the drying treatment, annealing treatment, and the like after film formation of metal alkoxide added with liquid repellency (water repellency and oil repellency). Preferably, before forming the liquid-repellent film **203**, surface reforming is performed on a face of the base film **202** by ultraviolet (UV) irradiation, a plasma treatment, an ozone treatment, and the like.

Any metal alkoxide that has water repellency and oil repellency may be used as a material but, preferably, metal alkoxide that contains a long-chain polymer group (hereinafter referred to as "long-chain RF group") containing fluorine or metal acid salt having a liquid-repellent group is used. Examples of the metal alkoxide are various, using Ti, Li, Si, Na, K, Mg, Ca, St, Ba, Al, In, Ge, Bi, Fe, Cu, Y, Zr, Ta, and the like, but silicon, titanium, aluminum, zirconium, and the like are commonly used. In this embodiment, what uses silicon, preferably, alkoxysilane that contains the long-chain RF group containing fluorine or the metal acid salt having a liquid-repellent group, is used.

Examples of the long-chain RF group include a perfluoroalkyl chain and a perfluoropolyether chain whose molecular weight is at least 1,000.

Examples of the alkoxysilane having the long-chain RF group include a silane coupling agent having the long-chain RF group.

Examples of the silane coupling agent having the long-chain RF group suitable for the film formation of the liquid-repellent film **203** include hepta-fluoro-thoria conta dieicosyl trimethoxysilane. Examples of products include Optool DSX (trademark, manufactured by Daikin Industries, Ltd.) and KY-130 (trademark, manufactured by Shin-Etsu Chemical Co., Ltd.).

A fluorocarbon group (RF group) has smaller surface free energy than an alkyl group, and thus the liquid repellency of the liquid-repellent film that is formed can be improved and properties such as chemical resistance, weather resistance, and abrasion resistance can be improved by allowing the metal alkoxide to contain the RF group. The liquid repellency can better last when the long-chain structure of the RF group is long. Further, examples of the metal acid salt having the liquid-repellent group include aluminate and titanate.

Next, the nozzle plate **20**, particularly processes of manufacturing the nozzle plate **20**, will be described in detail.

FIGS. **2**A to **2**D are schematic views showing the processes of manufacturing the nozzle plate **20**.

In this embodiment, the above-described silicon single crystal substrate (silicon substrate) **25** is used as the material of the nozzle plate **20**, and a plurality of the nozzle plates **20** are manufactured from the one substrate **25**. As shown in FIG. **2**A, the nozzle opening **21** formed from the first cylindrical portion **22** and the second cylindrical portion **23** is formed first by dry etching with respect to the silicon substrate **25**.

Next, as shown in FIG. **2**B, the silicon thermal oxide film **200** is formed by a heat treatment on a discharge side surface (surface on a lower side in the drawing, hereinafter referred to as "first surface") on the ink discharge side, the surface (surface on an upper side in the drawing, hereinafter referred to as "second surface") on the opposite side from the surface, and the inner circumferential surface of the nozzle opening **21**. The thermal oxide film **200** is formed of silicon dioxide, and the thickness thereof is approximately 100 nm.

A process of forming the thermal oxide film **200** may be omitted.

Next, as shown in FIG. **2**C, the protective film **201** formed of tantalum oxide is film-formed by the atomic layer deposition method on the first surface on the ink discharge side, the second surface, and the inner circumferential surface of the nozzle opening **21**. H_2O or O_3 is used as an oxidizing agent during the film formation of the tantalum oxide by the atomic layer deposition method, and the film formation temperature is 120° C. to 350° C. The thickness of the protective film **201** may be within a range of 0.3 Å to 50 nm, preferably within a range of 10 nm to 30 nm since the film formation by the atomic layer deposition method is uniform and fine (high film density). Ta_2O_5 (TaOx) is alkali-soluble but is unlikely to be alkali-soluble when the film density is high (approximately 7 g/cm^2) and, in terms of acid resistance, is not soluble in a solution other than hydrofluoric acid, and thus the protective film is effective against a strong alkaline liquid and a strong acid solution.

Subsequently, as shown in FIG. **2**D, the base film **202** formed from the tantalum oxide film is film-formed by plasma CVD on the protective film **201** of the first surface, surface reforming is performed on the face of the base film **202** by ultraviolet (UV) irradiation, the plasma treatment, the ozone treatment, and the like and then, thereon, the film formation of the molecular film of metal alkoxide having liquid repellency is performed. Then, the liquid-repellent film **203** is formed through the drying treatment, the annealing treatment, and the like. Compared to the ALD method, the film formation by plasma CVD has a significantly higher film formation rate, and the thick film can be easily performed. Preferably, the film thickness of the base film **202** is within a range of 200 nm to 1,000 nm.

Herein, compared to the protective film **201** and the base film **202**, the liquid-repellent film **203** has high electrical insulation, and thus is formed only in an area other than a conductive area in a case where a conductive member is installed on the first surface for conduction. With regard to the conductive area, the liquid-repellent film **203** and, if necessary, the base film **202** may be removed only in a related part after forming the liquid-repellent film **203** on the entire first surface, and the base film **202** and the liquid-repellent film **203** may be formed in the related part from the beginning by masking only the related part during the formation of the liquid-repellent film **203**.

After the liquid-repellent film **203** is formed, the silicon substrate **25** is divided such that the plurality of nozzle plates **20** are obtained. The nozzle plates **20** are manufactured through this process.

Embodiment 2

Hereinafter, an inkjet type recording head that is an example of a liquid ejecting head using the nozzle plate **20** of Embodiment 1 described above will be described.

FIG. **3** is an exploded perspective view of the ink jet type recording head of this embodiment, FIG. **4**A is a plan view of FIG. **3** and FIG. **4**B is a cross-sectional view taken along line A-A' of FIG. **4**A, and FIG. **5** is a cross-sectional view taken along line B-B' of FIG. **4**B.

As shown in the drawings, a passage forming substrate **10** of an ink jet type recording head I which is an example of the liquid ejecting head of this embodiment is formed from, for example, a silicon single crystal substrate in this embodiment. In the passage forming substrate **10**, pressure generating chambers **12** that are partitioned by a plurality of partition walls **11** are arranged along a direction in which a plurality of nozzle openings **21** discharging ink of the same color are arranged. Hereinafter, this direction is referred to as an arrangement direction of the pressure generating chambers **12** or a first direction X. Also, hereinafter, a direction that is orthogonal to the first direction X is referred to as a second direction Y.

Ink supply paths **13** and communication paths **14** are partitioned by the plurality of partition walls **11** on one longitudinal direction end portion side of the pressure generating chambers **12** of the passage forming substrate **10**, that is, one second direction Y end portion side orthogonal to the first direction X. Outside (opposite side from the pressure generating chambers **12** in the second direction Y) the communication paths **14**, a communication portion **15** that constitutes a part of a manifold **100** which is a common ink chamber (liquid chamber) of the pressure generating chambers **12** is formed. In other words, a liquid passage formed from the pressure generating chambers **12**, the ink supply paths **13**, the communication paths **14**, and the communication portion **15** is formed in the passage forming substrate **10**.

Herein, a liquid-resistant film **210** that is formed of a material having ink resistance (liquid resistance), for example, tantalum oxide (TaOx; amorphous) such as tantalum pentoxide, is disposed on an inner wall surface (inner surface) of the liquid pas sage of the passage forming substrate **10** formed from the pressure generating chambers **12**, the ink supply paths **13**, the communication paths **14**, and the communication portion **15**. A material of the liquid-resistant film **210** is not limited to tantalum oxide but, for example, oxide silicon (SiO_2), zirconium oxide (ZrO_2), hafnium oxide (HfO_2), nickel (Ni), chromium (Cr), and the like may be used depending on the pH value of the ink which is used.

The liquid-resistant film **210** can be formed by a gas phase method such as a sputtering method and an atomic layer deposition (ALD) method but, particularly, it is preferable that the liquid-resistant film **210** be formed by using the atomic layer deposition (ALD) method. By the atomic layer deposition method, the liquid-resistant film **210** can be formed to have a relatively thin film thickness and high film density. In other words, the ink resistance (liquid resistance) of the liquid-resistant film **210** can be improved and erosion of a vibration plate **50**, the passage forming substrate **10**, and the like by ink (liquid) can be suppressed by forming the liquid-resistant film **210** with high film density. Accordingly, the thickness of the liquid-resistant film **210** can be reduced. Also, compared to the CVD method and the like, the liquid-resistant film **210** can be formed to be thin by the atomic layer deposition method. However, the film formation by the atomic layer deposition method is time-consuming compared to the sputtering method and is not suitable for formation of a thick film.

The nozzle plate **20** of Embodiment 1 in which the nozzle openings **21** respectively communicating with the pressure generating chambers **12** are formed is bonded to one surface side of the passage forming substrate **10**, that is, a surface where the liquid passage of the pressure generating chambers **12** and the like is open, by an adhesive agent, a heat welding film, or the like. In other words, the nozzle openings **21** are arranged in the first direction X on the nozzle plate **20**.

An elastic film **51** that is formed of oxide silicon (SiO_2) formed by thermal oxidation, and an insulator layer **52** that is formed on the elastic film **51** and is formed of a material containing zirconium oxide (ZrO_2) are stacked on the other surface side of the passage forming substrate **10**. The liquid passage of the pressure generating chambers **12** and the like is formed by anisotropic etching of the passage forming substrate **10** from the one surface side (surface side bonded with the nozzle plate **20**), and the other surface of the liquid passage of the pressure generating chambers **12** and the like is defined by the elastic film **51**.

Piezoelectric actuators **300** that have a first electrode **60**, piezoelectric layers **70**, and second electrodes are formed on the insulator layer **52**. Herein, the piezoelectric actuator **300** refers to a part that has the first electrode **60**, the piezoelectric layers **70**, and the second electrodes **80** and, in general, is configured by any one electrode of the piezoelectric actuator **300** being a common electrode and by patterning the other electrode and the piezoelectric layer **70** for each of the pressure generating chambers **12**. Herein, a part that is configured to have any one patterned electrode and the piezoelectric layer **70** and where piezoelectric distortion is generated by voltage application to both of the electrodes is referred to as a piezoelectric active portion **320**. In this embodiment, the first electrode **60** is the common electrode of the piezoelectric actuator **300** and the second electrode **80** is an individual electrode of the piezoelectric actuator **300**, but this may be reversed for drive circuit and wiring convenience.

The piezoelectric layer **70** is formed of a piezoelectric material of oxide having a polarized structure formed on the first electrode **60** and, for example, can be formed of perovskite type oxide expressed by the general expression of ABO_3, in which A can contain lead and B can contain at least either one of zirconium and titanium. The above-described B can, for example, further contain niobium. Specifically, for example, lead zirconate titanate ($Pb(Zr, Ti)O_3$: PZT), silicon-containing lead zirconate titanate niobate ($Pb(Zr, Ti, Nb)O_3$: PZTNS), and the like can be used as the piezoelectric layer **70**.

The piezoelectric layer **70** may be a composite oxide or the like that has a perovskite structure containing a lead-free piezoelectric material not containing lead, for example, bismuth ferrite and bismuth manganese ferrite, and barium titanate and bismuth potassium titanate.

Further, a lead electrode **90** that is drawn out from the vicinity of an ink supply path **13** side end portion and extends onto the vibration plate **50**, which is formed of, for example, gold (Au), is connected to each of the second electrodes **80** which is the individual electrode of the piezoelectric actuator **300**.

A protective substrate **30** that has a manifold portion **31** constituting at least a part of the manifold **100** is bonded via an adhesive agent **35** onto the passage forming substrate **10** where the piezoelectric actuator **300** is formed in this manner, that is, onto the first electrode **60**, the vibration plate **50**, and the lead electrode **90**. In this embodiment, the manifold portion **31** penetrates the protective substrate **30** in a thickness direction and is formed across a width direction of the pressure generating chamber **12** and, as described above, communicates with the communication portion **15** of the passage forming substrate **10** to constitute the manifold **100** that is a common ink chamber of the pressure generating chambers **12**. Also, only the manifold portion **31** may be the manifold by dividing the communication portion **15** of the passage forming substrate **10** into a plurality of portions for the pressure generating chambers **12**. Further, for example, only the pressure generating chambers **12** may be disposed in the passage forming substrate **10** and the ink supply path **13** that causes the manifold and each of the pressure generating chambers **12** to communicate with each other may be disposed in the vibration plate **50** that is interposed between the passage forming substrate **10** and the protective substrate **30**.

A piezoelectric actuator holding unit **32** that has a space to an extent to which a movement of the piezoelectric actuator **300** is not inhibited is disposed in an area of the protective substrate **30** opposing the piezoelectric actuator **300**. The piezoelectric actuator holding unit **32** may have the space to the extent to which the movement of the piezoelectric actuator **300** is not inhibited, and the space may be sealed or may not be sealed.

A through-hole **33** that penetrates the protective substrate **30** in the thickness direction is disposed in the protective substrate **30**. The vicinity of an end portion of the lead electrode **90** that is drawn out from each of the piezoelectric actuators **300** is disposed to be exposed into the through-hole **33**.

A drive circuit **120** that functions as a signal processing unit is fixed onto the protective substrate **30**. For example, a circuit substrate, a semiconductor integrated circuit (IC), and the like can be used as the drive circuit **120**. The drive circuit **120** and the lead electrode **90** are electrically connected to each other via connection wiring **121** that is formed of a conductive wire such as a bonding wire which is inserted into the through-hole **33**.

Preferably, a material of the protective substrate **30** has a coefficient of thermal expansion substantially equal to a coefficient of thermal expansion of the passage forming substrate **10** such as glass and a ceramic material and, in this embodiment, the material is a silicon single crystal substrate which is the same material as the passage forming substrate **10**.

A compliance substrate **40** that is formed from a sealing film **41** and a fixed plate **42** is bonded onto the protective substrate **30**. Herein, the sealing film **41** is formed of a low-rigidity material having flexibility, for example, a polyphenylene sulfide (PPS) film, and one surface of the manifold portion **31** is sealed by the sealing film **41**. The fixed plate **42** is formed of a hard material such as metal, for example, stainless steel (SUS). An area of the fixed plate **42** opposing the manifold **100** has an opening portion **43** that is completely removed in the thickness direction, and thus one surface of the manifold **100** is sealed only by the sealing film **41** that has flexibility.

In the ink jet type recording head I of this embodiment, ink is taken in from an ink introduction port connected to an outer ink supply unit which is not shown and an inner portion ranging from the manifold **100** to the nozzle openings **21** is filled with the ink, then voltage is applied between each of the first electrode **60** and the second electrodes corresponding to the pressure generating chambers **12** according to a recording signal from the drive circuit **120**, and the vibration plate **50**, the first electrode **60**, and the piezoelectric layer **70** are deflected such that pressure within each of the pressure generating chambers **12** is increased and ink drops are discharged from the nozzle openings **21**. As described above, the ink jet type recording head I of this embodiment includes the nozzle plate **20** of Embodiment 1, and thus has excellent ink resistance and can uniformly discharge ink drops. In other words, the protective film **201** that is formed from the tantalum oxide film which is formed by atomic layer deposition is formed on both of the surfaces of the nozzle plate **20** and the inner circumferential surface of the nozzle opening **21**, and the base film **202** containing tantalum oxide by plasma CVD and the liquid-repellent film **203** are formed on the discharge surface thereon such that the uniform protective film **201** formed from the tantalum oxide film is formed on an inner surface of the nozzle opening **21**, particularly around the vicinity of the discharge surface to have excellent ink resistance. The protective film **201** that is formed from the tantalum oxide film is formed to be uniform and into a relatively thin film on the inner circumferential surface of the nozzle opening **21** such that there is no problem of non-uniformity of the discharged ink drops. Further, the thick tantalum oxide film is formed on the protective film **201** as the base film **202** of the liquid-repellent film **203** such that a circumferential edge portion of the nozzle opening **21** of the discharge surface is covered by the base film **202** and the liquid resistance is even more excellent and the abrasion resistance is excellent.

Another Embodiment

Hereinabove, Embodiments 1 and 2 of the invention have been described, but a basic configuration of the invention is not limited to the above description.

In Embodiment 2 described above, the thin film type piezoelectric actuator **300** is used as a pressure generation unit that discharges ink drops from the nozzle openings **21**, but the invention is not limited thereto. For example, a thick film type piezoelectric actuator formed by a method of attaching a green sheet or the like, and a longitudinal vibration type piezoelectric actuator in which a piezoelectric material and an electrode forming material are alternately stacked and are extended and retracted in an axial direction may be used.

In Embodiment 2 described above, the thin film type piezoelectric actuator **300** is used as the pressure generation unit that generates a pressure change in the pressure generating chamber **12**, but the invention is not limited thereto. For example, the thick film type piezoelectric actuator formed by the method of attaching the green sheet or the like, the longitudinal vibration type piezoelectric actuator in which the piezoelectric material and the electrode forming material are alternately stacked and are extended and retracted in the axial direction, and the like may be used. Also, as the pressure generation unit, what discharges liquid drops from a nozzle opening by using bubbles generated by heat generation of a heat generating element arranged in a pressure generating chamber, a so-called electrostatic actuator that generates static electricity between a vibration plate and an electrode, deforms the vibration plate by electrostatic force, and discharges liquid drops from a nozzle opening, and the like can be used.

In Embodiment 2 described above, the silicon single crystal substrate is used as an example of the passage forming substrate **10**, but the invention is not limited thereto. For example, a material such as an SOI substrate and glass may be used.

In addition, the ink jet type recording head of each of the embodiments constitutes a part of a recording head unit including an ink passage communicating with an ink cartridge and the like, and is mounted on inkjet type recording apparatus. FIG. **6** is a schematic view showing an example of the ink jet type recording apparatus.

As shown in FIG. **6**, recording head units **1**A and **1**B including the inkjet type recording head are disposed in such a manner that cartridges **2**A and **2**B constituting the ink supply unit are removable. A carriage **3** on which the recording head units **1**A and **1**B are mounted is disposed in a carriage shaft **5** installed in an apparatus main body **4** in an axially movable manner. The recording head units **1**A and **1**B respectively discharge, for example, a black ink composition and a color ink composition.

When drive force of a drive motor **6** is transmitted to the carriage **3** via a plurality of not-shown gears and a timing belt **7**, the carriage **3** on which the recording head units **1**A and **1**B are mounted is moved along the carriage shaft **5**. A platen **8** is disposed in the apparatus main body **4** along the carriage shaft **5**, and a recording sheet S that is a recording medium such as paper which is fed by a not-shown paper feed roller or the like is transported wound around the platen **8**.

In addition, in the above-described ink jet type recording apparatus II, the ink jet type recording head I (recording head units **1**A and **1**B) is mounted on the carriage **3** and is moved in a main scanning direction, but the invention is not limited thereto. For example, the invention can also be applied to a so-called line type recording apparatus in which the ink jet type recording head I is fixed and printing is performed only by moving the recording sheet S such as paper in a sub-scanning direction.

In the above-described embodiments, the ink jet type recording head is used as an example of the liquid ejecting head and the ink jet type recording apparatus is used as an example of the liquid ejecting apparatus. However, the invention covers a wide variety of liquid ejecting heads and liquid ejecting apparatuses and, as a matter of course, can be applied to liquid ejecting heads and liquid ejecting apparatuses ejecting liquids other than ink. Examples of the other liquid ejecting heads include various types of recording heads used in image recording apparatuses such as printers, coloring material ejecting heads used in manufacturing color filters such as liquid crystal displays, electrode material ejecting heads used in forming electrodes such as organic EL displays, field emission displays (FED), and bio-organic material ejecting heads used in manufacturing biochips. The invention can also be applied to liquid ejecting apparatuses including such liquid ejecting heads.

The entire disclosure of Japanese Patent Application No. 2012-284499, filed Dec. 27, 2012 is expressly incorporated by reference herein.

What is claimed is:

1. A nozzle plate comprising:

a silicon substrate;

a plurality of nozzle openings which are disposed in the silicon substrate;

a first tantalum oxide film which is formed by atomic layer deposition and disposed on a discharge surface and an upper surface of the silicon substrate and an inner surface of the nozzle opening; and

a second tantalum oxide film which is stacked by plasma CVD on the portion of the first tantalum oxide film that is disposed on the discharge surface,

wherein the combination of the portion of the first tantalum oxide film that is disposed on the discharge surface and the second tantalum oxide that is stacked on the portion of the first tantalum oxide film that is disposed on the discharge surface is thicker than the portion of the first tantalum oxide film that is disposed on the upper surface.

2. The nozzle plate according to claim **1**,

wherein a thickness of the first tantalum oxide film formed by the atomic layer deposition is within a range of 0.3 Å to 50 nm, and a thickness of the second tantalum oxide film formed by the plasma CVD is within a range of 200 nm to 1,000 nm.

3. A liquid ejecting head comprising:

the nozzle plate according to claim **2**;

a passage forming substrate where a pressure generating chamber that is bonded with the nozzle plate and communicates with the nozzle opening is disposed; and

an actuator that is disposed on an opposite side to the nozzle plate of the passage forming substrate to generate a pressure change in the pressure generating chamber.

4. A liquid ejecting apparatus comprising the liquid ejecting head of claim **3**.

5. The nozzle plate according to claim **1**,

wherein a silicon thermal oxide film is formed in a lower layer of the first tantalum oxide film formed by the atomic layer deposition.

6. A liquid ejecting head comprising:

the nozzle plate according to claim **5**;

a passage forming substrate where a pressure generating chamber that is bonded with the nozzle plate and communicates with the nozzle opening is disposed; and

an actuator that is disposed on an opposite side to the nozzle plate of the passage forming substrate to generate a pressure change in the pressure generating chamber.

7. A liquid ejecting apparatus comprising the liquid ejecting head of claim **6**.

8. The nozzle plate according to claim **1**,

wherein a liquid-repellent film is stacked on the second tantalum oxide film formed by the plasma CVD through annealing of a metal alkoxide film.

9. A liquid ejecting head comprising:

the nozzle plate according to claim **8**;

a passage forming substrate where a pressure generating chamber that is bonded with the nozzle plate and communicates with the nozzle opening is disposed; and

an actuator that is disposed on an opposite side to the nozzle plate of the passage forming substrate to generate a pressure change in the pressure generating chamber.

10. A liquid ejecting apparatus comprising the liquid ejecting head of claim **9**.

11. A liquid ejecting head comprising:

the nozzle plate according to claim **1**;

a passage forming substrate where a pressure generating chamber that is bonded with the nozzle plate and communicates with the nozzle opening is disposed; and

an actuator that is disposed on an opposite side to the nozzle plate of the passage forming substrate to generate a pressure change in the pressure generating chamber.

12. A liquid ejecting apparatus comprising the liquid ejecting head of claim **11**.

13. The nozzle plate according to claim **1**, wherein the second tantalum oxide film is only disposed on the discharge surface.

14. The nozzle plate according to claim **1**, wherein the second tantalum oxide film is directly stacked on the first tantalum oxide film.

15. The nozzle plate according to claim **1**, wherein a film density of the first tantalum oxide film is higher than a film density of the second tantalum oxide film.

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